A comparison of the figures of merit for nitrogen reduction on nitrogenase, solid electrodes and homogeneous catalysts

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This document estimates the operating potentials on the RHE scale, the turnover frequencies (TOF) and turnover numbers (TON) for four different electrochemical nitrogen reduction systems over a solid electrode[1–4], the Schrock homogeneous catalyst for nitrogen reduction[5] and nitrogenase. An idealised target electrode is also considered. This formulation allows for greater ease of comparison between homogeneous systems, enzymes and solid electrodes.

1. Potential calculation on the RHE scale: solid electrodes

$$\mathrm{N_2 + 6H^+ + 6e^- \rightarrow 2NH_{3(g)}}$$

Equilibrium potential for N_2 reduction to $NH_{3(g)}$:

$$U^0 = -\frac{RT}{nF} lnK$$

R = universal gas constant [J mol^{-1} K^{-1}], T = temperature [K], n = moles of electrons, F = Faraday constant [C mol^{-1}], K = equilibrium constant

$$K = exp\left(\frac{\Delta G_{NH3(g)}}{RT}\right)$$

$\Delta G_{NH3(g)}$ = -16.4 kJ mol^{-1} = -16.4 x 10^3 C V mol^{-1} [6] (Standard molar Gibbs energy of formation)

$$U^0 = -\frac{\Delta G_{NH3(g)}}{3F} = 0.057\ RHE$$

This equilibrium potential would be different for a solution species, depending on the solubility of $NH_{3(g)}$ and the pK_a of the solution. However, regardless of the reference state and its activity, that the standard potential does not change appreciably (on the order of a few hundred millivolts), relative to the RHE potential[7].

Lazouski et al[4] show that the reversible potential for H_2 evolution/oxidation occurs at -0.7 V vs Fc$^+$/Fc and -0.3 V vs Ag/AgCl. Thus, for Ag/AgCl, let U^0_{RHE}=-0.3 V vs Ag/AgCl. Therefore 0 V vs Ag/AgCl = 0.3 V vs RHE For Fc$^+$/Fc, let U^0_{RHE}=-0.7 V. Therefore 0 V vs Fc$^+$/Fc = 0.7 V vs RHE.

Lazouski et al report Li plating at ~ -3 V vs Ag/AgCl, which is therefore -2.7 V vs RHE.

This value is appropriate for the Lazouski electrolyte (0.11 M EtOH and 1 M $LiBF_4$ in THF). For other electrolytes, the potential for lithium plating will depend on the activity of protons and lithium cations, as well as the solvation energy of lithium cations[8].

Andersen et al[2] (2019) use an electrolyte made up of 0.2 M $LiClO_4$ in a mixture of 99:1 (vol) THF:EtOH.

Andersen et al[3] (2020) use an electrolyte made up of 0.3 M $LiClO_4$ in a mixture of 99:1 (vol) THF:EtOH.

Suryanto et al[1] (2021) used 0.2 M $LiBF_4$, 0.1 M $[P_{6,6,6,14}]$[eFAP] in THF.

It will now be evaluated whether or not it is reasonable to use the same lithium plating potential vs RHE for all the electrolytes as for that measured by Lazouski et al[4].

1. **a. Hydrogen evolution:**

$$2H^+ + 2e^- \rightarrow H_2$$

The potential depends on the activity of protons as

$$U = U^0 + \frac{RT}{F} ln(a_{H^+}).$$

The Ag/AgCl electrode potential $U_{Ag/AgCl}$ +0.197 - 0.0591 x pH vs Ag/AgCl =U_{RHE} vs RHE.
In the Lazouski electrode, $U_{Ag/AgCl}$ = -0.3 V vs Ag/AgCl = U_{RHE} vs RHE = 0 V vs RHE
Therefore, *pH* = (0.3-0.197)/-0.0591=-1.74, a_{H^+}=5.71.

When *U* = 0, $U^0 = -\frac{RT}{F} ln(a_{H^+}), \therefore U^0 = -0.04V.$

Lazouski et al use an ethanol concentration of 0.11 M EtOH. Andersen et al (2019)[2] use a concentration of 1% vol in 8 ml electrolyte, which is a concentration of 0.17 M EtOH. They use the same molar concentration for their 2020 paper[3]. Assume that activity has the same linearity constant to activity in both electrolytes.

$$\frac{a_{H^+}(Lazouski)}{a_{H^+}(Andersen)} = \frac{[EtOH]_{Lazouski}}{[EtOH]_{Andersen}}$$

This gives $a_{H^+}(Andersen)$ = 8.8, pH = -0.95. This change in activity would shift the equilibrium potential of hydrogen evolution to -0.05 V, which is negligible given the magnitude of the potentials involved.

Suryanto et al[1] used a different electrolyte (0.2 M $LiBF_4$, 0.1 M $[P_{6,6,6,14}]$[eFAP] in THF). Clyburne and co workers[9] state the pKa of ylides as 8 – 11. Let the pKa of the $[P_{6,6,6,14}]$[eFAP] be 9.5, so $K_a = 3.16x10^{-10}$.

Use the following logic to obtain the proton concentration:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$[H^+] = [A^-], \therefore K_a = \frac{[H^+]^2}{[HA]}$$

Therefore, $[A^-] = [H^+] = (0.1\ x\ 3.16\ x\ 10^{-10})^{0.5}$ = 5.62 x 10^{-6}. The pH is given by

$$pH = pK_a + log\frac{[A^-]}{[HA]},$$

So the pH is 5.25 (much more basic than the other electrolytes), and the activity of protons, $a_{H^+}(Suryanto)$ = 5.25 x 10^{-3}. This would give U^0= 0.13 V vs RHE. This is a shift of 0.17 V, which means that it is not completely accurate to use the same RHE potential shift as for Lazouski et al. The potential for Suryanto et al will be calculated separately.

1. b. Lithium plating:

Lithium plating follows the below relationship.

$$Li^+ + e^- \rightarrow Li_s$$

$$U = U^0 + \frac{RT}{F} ln\ a\{Li^+\}$$

$$U^0 = -\frac{RT}{F} ln(a_{Li^+})$$

Let U^0 = -2.7 V vs RHE (i.e. assume negligible overpotential) in the Lazouski electrolyte. This is not entirely unreasonable, since the standard potential for Li reduction in other organic solvents varies between -2.9 and -3.5 vs RHE[10]. Therefore a_{Li^+} = 2.76 x 10^{46} in the Lazouski electrolyte.

1. b. i. Effect of solvent components

For a metal redox reaction, the variation in the standard potential in different electrolytes is related to the solvation energy of the metal ion in that solvent. If the metal ion is more strongly solvated, the standard potential will be more negative. The standard potential measured in solvents 1 and 2 will vary as

$$U^0(1) - U^0(2) = -\frac{RT}{nF}(ln\ a\{M^{n^+}, 1\} - ln\ a\{M^{n^+}, 2\}) = \frac{RT}{nF} ln\gamma_t(M^{n^+}, 1 \rightarrow 2),$$

where $\gamma_t(M^{n^+}, 1 \rightarrow 2)$ is the transfer activity coefficient of M^{n^+} from solvent 1 to 2. This is given by

$$ln\ \gamma_t(M^{n^+}, 1 \rightarrow 2) = \Delta G_t^0(M^{n^+}, 1 \rightarrow 2)/(2.303RT),$$

Where $\Delta G_t^0(M^{n^+}, 1 \rightarrow 2)$is the Gibbs energy of transfer between solvents 1 and 2[10]. Therefore,

$$U^0_{H_2O} - U^0_{Lazouski} = \frac{1}{2.303F} \Delta G_t^0(Li^+, H_2O \longrightarrow Lazouski).$$

The standard reduction potential for Li is in water U^0_{H2O}= -3.040 V vs SHE = -3.040 + 0.0591 x pH vs RHE = -2.6 vs RHE (pH 7) [11].

Take standard reduction potential for Li to be U^0 = -2.7 V vs RHE in the Lazouski et al (2020) electrolyte. This gives the Gibbs free energy of transfer as $\Delta G_t^0(Li^+, H_2O \longrightarrow Lazouski)$=-22.2 kJ mol^{-1}.

For H_2O to EtOH, $\gamma_t(Li^+, H_2O \rightarrow EtOH) = 1.9.$ [10] Therefore $\Delta G_t^0(Li^+, H_2O \rightarrow EtOH)$ = 3.60 kJ mol^{-1}.

The Lazouski solvent is made up of 0.11 M EtOH in THF. 1.75ml of electrolyte solution was added to the working electrode compartment. This equates to a volume of 0.0112 ml EtOH, which is 0.64 % (vol).

Since the Gibbs free energy change is a linear combination of enthalpy and entropy, let $\Delta G_t^0(Li^+, H_2O \longrightarrow \text{Lazouski}) = \%\, vol\, EtOH \cdot \Delta G_t^0(Li^+, H_2O \rightarrow EtOH) + \%\, vol\, THF \cdot \Delta G_t^0(Li^+, H_2O \rightarrow THF)$

Therefore, $\Delta G_t^0(Li^+, H_2O \rightarrow THF)$ = 22.08 kJ mol^{-1}.

The Andersen electrolyte contained 1% EtOH in THF[2,3]. Using the same logic as above, this gives $\Delta G_t^0(Li^+, H_2O \rightarrow Andersen)$ = 22.09 kJ mol^{-1}. To find the activity of Li^+ and the standard potential, the following logic is applied:

$$\Delta G_t^0(Li^+, H_2O \longrightarrow Lazouski) - \Delta G_t^0(Li^+, H_2O \longrightarrow Andersen) = -2.303\, RT(ln\, a\{Li^+, \text{Andersen}\} - ln\, a\{Li^+, \text{Lazouski}\})$$

This gives $ln(a_{Li^+,\text{Andersen}}) = 106.9$, $a_{Li^+,\text{Andersen}} = 2.76 \times 10^{46}$, U^0= -2.70 V vs RHE. Therefore, the change in ethanol concentration between the two electrolytes does not significantly change the potential for lithium reduction.

1. b. ii. Effect of lithium ion concentration

However, the above argument assumes the same concentration of Li^+ ions. Of course, this is not correct since Andersen et al used between 0.2 and 0.3 M $LiClO_4$ and Lazouski et al used 1 M $LiBF_4$. If we assume that activity is linearly proportional to molar concentration of lithium salt and is independent of anion, we find that $a_{Li^+,\text{Andersen2019}}$=5.52 x 10^{45} and $a_{Li^+,\text{Andersen2020}}$=8.28 x 10^{45}. This results in reduction potentials of

$$U^0_{Andersen,\ 2019} = -2.66\, V\, vs\, RHE$$

and

$$U^0_{Andersen,\ 2020} = -2.67\, V\, vs\, RHE$$

for the two papers respectively. Therefore, changing the salt concentration does not significantly change the potential for lithium reduction.

1. b. iii. Effect of lithium anion

However, the above arguments do not account for any contribution from the counteranion; Lazouski et al used 1M $LiBF_4$ and Andersen et al used either 0.2 or 0.3 M $LiClO_4$. However, the counteranion are more likely to be in the solvation shell of the Li^+ cation when the salt concentration is high[12]. The concentrations considered here are low enough that this can be neglected.

Since the lithium plating and reversible hydrogen oxidation/evolution potentials are not found to vary significantly between the different electrolytes when different parameters are changed, let the lithium plating potential be -2.7 V vs RHE for Andersen et al (2019 and

2020). Since all Li mediated systems operate at Li plating potentials, let the operating potential be -2.7 V vs RHE (except Suryanto et al).

Note, in many cases this is a minimum value since the working electrode potential drifts to more negative potentials over time.

Suryanto et al[1] calculated their Li^+ redox potential to be -3.06 V vs SHE. Since the pH was estimated to be 5.24, the RHE potential for Li reduction is -3.06 + 0.0591 x pH V vs RHE = -2.75 V vs RHE

For the 20h experiments, the authors operated at -0.75 V vs Li/Li^+, which would be -3.5 V vs RHE. However, they did not correct for ohmic drop. They report the resistance of their electrolyte as 525 Ω (average of n=3). The electrode area was 0.012 cm^2. For the 20h experiments, the current density was -22.5 mA cm^{-2}, so the ohmic drop is -0.14 V. Therefore, the potential is -3.36 V vs RHE.

2. Potential calculation on the RHE scale: Nitrogenase – assumptions and definitions

Value of -0.8 V vs RHE taken from Varley et al[13].
See Bukas and Norskov[14] for a rigorous calculation which arrives at a value of -1.1 V vs SHE. At pH 7, this is equivalent to -0.68 V vs RHE, which is similar to Varley et al.

3. Potential calculation on the RHE scale: homogeneous systems

Yandulov and Schrock[5] used 36 equivalents of $CrCp^*_2$ as a reducing agent and 48 equivalents of $\{LutH\}\{BAr^F_4\}$ as a proton source in heptane. 10 ml of a solution of $CrCp^*_2$ in heptane was added at a rate of 1.7 ml/hour to a 0.6 ml solution of $\{LutH\}\{BAr^F_4\}$, the catalyst and heptane.

Bosch and co-workers define the pKa of 2,6 Lutidine as 9.5 in THF[15].
Bosch and coworkers use the following method to convert pKa in different solvents

$$pK_a(S1) = a \cdot p(S2) + b,$$

where *a* and *b* are empirically defined constants[15].
Therefore, the pKa of acids in one solvent is directly proportional to their value in another solvent, as shown by Leito and coworkers[16]. Leito and co-workers have data to transform between heptane (C7) and acetonitrile (MeCN), and MeCN and THF. Therefore, to transform between C7 and THF, use the following:

$$pK_a(THF) = a_1 \cdot pK_a(MeCN) + b_1$$
$$pK_a(C7) = a_2 \cdot pK_a(MeCN) + b_2$$
$$pK_a(C7) = x \cdot pK_a(THF) + y$$
$$x = \frac{a_2}{a_1}, y = -\frac{a_2}{a_1} b_1 + b_2$$

From figure S1, $a_1 = 0.6 \pm 0.2$, $b_1 = 4 \pm 3$, $a_2 = 1.0 \pm 0.3$, $b_2 = -20 \pm 5$. Therefore $x = 1.7 \pm 0.7$, $y = -27 \pm 8$

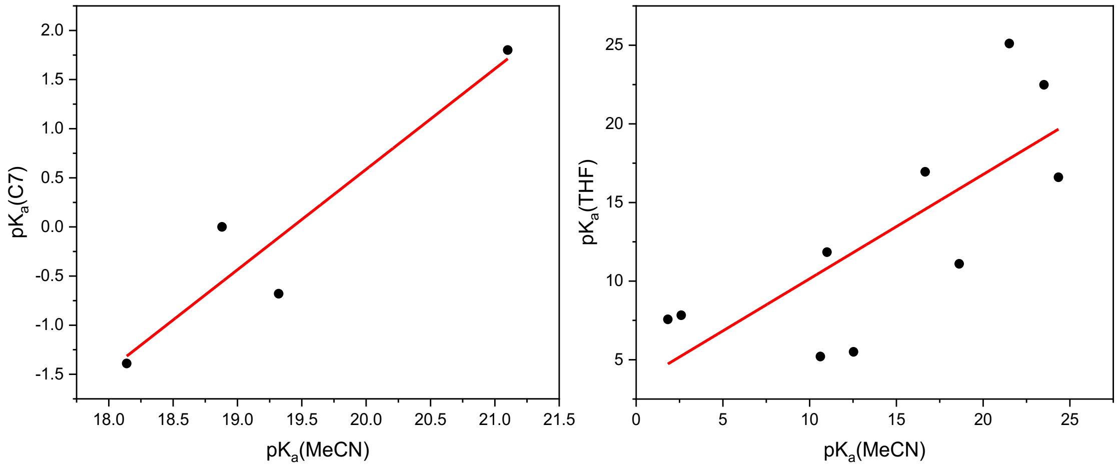

Figure 1: plots of the pKa values of some acids in solvents from reference [16].

Therefore, the pK_a of 2, 6 lutidine in heptane is -10.9 and K_a = 7.9 x 10^{10}. Given that the initial 0.6 ml solution would have been diluted over the course of the experiment, the activity of protons in solution would have decreased over time. Take the value for the final solution (10.6 ml). Schrock and Yandulov used an average of 5.87 µmol Mo compound and 48 equivalents of {LutH}{BAr$^F{}_4$}, which is 2.304 mmol. This results in a molar concentration of 0.22 M.

Use the following logic to obtain the pH:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$$let\ [H^+] = [A^-], \therefore K_a = \frac{[A^-]^2}{[HA]}$$

$$pH = pK_a + log\frac{[A^-]}{[HA]},$$

Therefore, the pH = -5.1.

Davis and coworkers[17] report the standard potential of CrCp*$_2$ as -1.47 vs Fc/Fc$^+$ in 0.4 M [Bu$_4$N][PF$_6$] in THF.

The Fc/Fc$^+$ potential vs SCE is reported as 0.56 vs SCE in a 0.1 M [Bu$_4$N][PF$_6$] in THF electrolyte.

The conversion from SCE to RHE is $U_{(RHE)} = U_{(SCE)} + 0.241 + 0.0591{*}pH$ V vs RHE.

[Bu$_4$N][PF$_6$] has an pK$_a$ of 5.57, and so K$_a$=2.7x10^{-6} [18]. Therefore pH = 3.3, so the Fc/Fc$^+$ potential is 1.0 V vs RHE in 0.1 M [Bu$_4$N][PF$_6$] in THF. This is 0.80 + 0.0591 x pH V vs RHE.

The pH of the 0.4 M [Bu$_4$N][PF$_6$] in THF electrolyte is 3.0. Therefore the Fc/Fc$^+$ potential is 0.98 V vs RHE in the 0.4 M [Bu$_4$N][PF$_6$] in THF electrolyte. Therefore, the CrCp*$_2$ potential is -0.49 V vs RHE at pH 3, which is -0.67 + 0.0591 x pH V vs RHE

Therefore, the operating potential vs RHE for Yandulov and Schrock was -0.97 V vs RHE.

4. TOF calculation: Solid electrodes

Given that the active site remains elusive in the lithium mediated system, assume that the active site is a Li atom in Li_3N[19].

Cell volume Li_3N = 44.57 Å^3, Laue class 6/mmm
Unit cell contains 3 Li atoms, 1 N atoms
a = 3.64 Å, b = 3.64 Å, c = 3.87 Å. $\alpha = 90°$, $\beta = 90°$, $\gamma = 120°$
(001) plane contains 1 Li atom, ¼ N atom, area unit cell = $3.64^2\sin(120)$ = 11.47 Å^2 [20].
Therefore, assuming close packing, the area occupied by Li =9.18 Å^2 = $9.18\text{x}10^{-16}$ cm^2.
Therefore, 1 cm^2 of Li_3N (001) contains $9.18\text{x}10^{16}$ atoms of Li

Define TOF as the number of catalytic turnovers per active site per second. 1 catalytic turnover is defined as the production of 1 molecule of ammonia, following the hypothesis that 1 mol NH_3 = N_A molecules NH_3.

1 µmol h^{-1} cm_{geo}^{-2} ≡ N_A x 10^{-6} / 60^2 x $9.18\text{x}10^{16}$ catalytic turnovers s^{-1} $site^{-1}$

Note that some papers did not quote the experiment length exactly. In such cases, an approximate experiment length was used from the data provided.

Reference	System	yield rate (µmol h^{-1} cm_{geo}^{-2})	TOF (catalytic turnovers s^{-1} $site^{-1}$)
Andersen et al, 2019[2]	Li_xN ($LiClO_4$ salt)	0.75 (average of NMR and Indophenol)	1.37 x 10^{-3}
Andersen et al, 2020[3]	Li_xN ($LiClO_4$, cycling, 10 bar N_2, 125 hours)	0.91	1.65 x 10^{-3}
Suryanto et al, 2021[1]	LixN ($LiBF_4$ & [$P_{6,6,6,14}$][eFAP], 20 bar N_2, 20 hours)	216	0.394

Lazouski et al, 2020[4] quote 8.8 mA cm^{-2} partial current density, 14mm diameter electrode → A = 1.54 cm^2

Current density to ammonia is given by:

$$i = \frac{3enN_A}{tA}$$

t = time [s], A = area of electrode [cm^2], N_A = Avogadro's number, n= mol NH_3

TOF ≡ number of ammonia molecules produced s^{-1} $site^{-1}$ = nN_A/t x (number of sites)
Number of sites = $9.18\text{x}10^{16}$ cm^{-2}
$\rightarrow i = \frac{3e*TOF*9.18\ x\ 10^{16}}{A}$
TOF = 2.82 x 10^{16} s^{-1} cm^2 = 0.31 s^{-1} $site^{-1}$

5. TOF calculation: Nitrogenase – assumptions and definitions

A catalytic turnover for nitrogenase is defined as one iteration of the equation:

$$\mathrm{N_2 + 8H^+ + 16MgATP + 8e^- \rightarrow 2NH_3 + H_2 + 16MgADP + 16Pi.} \quad 1$$

Seefeldt et al[21] state that Pi release is the rate limiting step for electron transfer in nitrogenase, occurring with a rate of 25 s^{-1}. 8 electron transfer steps are required to complete equation 1, which results in a TOF of 3.1 s^{-1} .

6. TOF calculation: Homogeneous catalysts

Schrock and Yandulov[5] report an average yield of 7.81 equivalents of NH_3 based on the catalyst, which is taken to be the number of turnovers, and a total experiment length of 6.88 hours.

The TOF is taken to be the TON divided by experiment time [s]. This gives a turnover frequency of 3.2×10^{-4} s^{-1} $site^{-1}$.

7. Faradaic efficiency: Solid electrodes

Used as reported in the papers:

Andersen et al, 2019: 6.5%
Andersen et al, 2020: 33.1%
Lazouski et al, 2020: 35%
Suryanto et al, 2021: 78%

8. Faradaic efficiency: Nitrogenase

Rivera-Ortiz and Burris[22] found that H_2 evolution has a Faradaic efficiency of 35% when nitrogenase is under 1 bar N_2. Assuming no other side reactions, this results in a 65% Faradaic efficiency towards ammonia.

9. Faradaic efficiency: homogeneous systems

Schrock and Yandulov[5] report yield efficiency based on the reductant, which is taken to be equivalent to Faradaic efficiency: 65%

10. TON: homogeneous catalysis

Schrock and Yandulov[5] report an average yield of 7.81 equivalents of NH_3 based on the catalyst, which is taken to be the number of turnovers.

11. TON: nitrogenase

Simon et al[23] report that the half life of mRNAs in wild type *Klebsiella pneumonia* nitrogenase is 20 to 30 mins. Take nitrogenase lifetime as 30 mins.

TON = TOF x experiment length [s] = 3.1 x 30 x 60 = 5580

12. TON: solid electrode

TON = TOF x experiment length [s] per site

Andersen et al, 2019[2]: $^{14}N_2$ open circuit test run for 1.5 hours. Assume that this is the same length as the electrochemical tests. TON = 0.00137 x 1.5 x 60^2 = 7.4 $site^{-1}$

Lazouski et al, 2020[4]: Longer duration experiments: produced 102 µmol NH_3 over 130 min, FE = 18.9%, 1 cm^2 electrode.

TON = yield (mol) *N_A / electrode area x 9.18×10^{16} = 668.9 $site^{-1}$

Andersen et al, 2020[3]: 743 $site^{-1}$ for 10 bar N_2, 125 hours.

Suryanto et al, 2021[1]: For 20 hr, 20 bar N_2 : 28344 $site^{-1}$

13. Targets:

The 'ideal electrode': 100% Faradaic efficiency, geometric current density 1 A cm^{-2}, 10mV overpotential, roughness factor 33.

$$\text{Roughness factor}=\frac{\text{real surface area}}{\text{projected surface area}}$$

$$\text{Actual current density}=\frac{\text{geometric current density}}{\text{roughness factor}}$$

Therefore, the actual current density ~ 30 mA cm^{-2}.

Assume site density of Ru(001) surface. Ru has Laue class 6/mmm.
a=2.8 Å, b = 2.8 Å, c=4.4 Å, α = 90°, β =90°, γ = 120°. [24]
(001) plane contains 1 atom Ru. Area = $2.8^2\sin(120)$ = 6.79 $Å^2$
Assuming close packing, let 1 cm^2 Ru(001) contain 2.17×10^{14} Ru atoms.

TOF = 6.25×10^{16} s^{-1} cm^{-2} = 288 s^{-1} $site^{-1}$
TON after 5 years for a 1 cm^2 electrode = 9.06×10^9 $site^{-1}$
Operating potential: -0.047 V vs RHE

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